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HYDROGEN SENSORS USING TAPERED OPTICAL FIBER COATED WITH METAL OXIDE NANOSTRUCTURES SYNTHESIZED VIA CHEMICAL BATH DEPOSITION TECHNIQUE

NOR AKMAR BINTI MOHD YAHYA

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By

NOR AKMAR BINTI MOHD YAHYA

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July 2018

Chairman : Mohd Hanif Yaacob, PhD
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In this thesis, novel optical hydrogen (H_2) sensors based on manganese dioxide (MnO_2), zinc oxide (ZnO) and molybdenum trioxide (MoO_3) nanostructures coated on tapered multimode fiber (MMF) via chemical bath deposition (CBD) were developed and investigated. The use of H_2 as a clean fuel in various application requires practical and robust sensors as to minimize the risk of explosions associated with its volatile properties. Semiconducting metal oxides (SMO) has been widely used for decades in H_2 sensing purpose due to its simplicity in fabrication, low cost and high sensitivity. Nanostructures SMO thin films as sensing layer has been reported to enhance the sensitivity of the sensors due to its high surface area to increase the gas molecules-sensing layer interaction. Typical SMO gas sensors are electrical based in which conductivity changes as it reacts to H_2 gas. However, it has certain limitations such as easily affected by electromagnetic interference (EMI) thus compromise the signal response and small sparks could ignite massive explosion if the H_2 concentration leaks is more than 4% in the environment. On the other hand, optical sensor which has yet well explored, offers advantages in term of size, light weight, resistant to EMI and resilient in high temperature environment. By integrating the optical transducer with SMO material, it can be employed as a hydrogen gas sensor. There are various methods of producing SMO material such as chemical and physical vapor deposition, RF sputtering, electrochemical deposition and thermal evaporation. These techniques require complicated setup with high operating temperature along with carrier gas during the process and need conductive substrate to perform the procedure. These techniques were also difficult to be implemented on optical fiber. Alternatively, chemical bath deposition method provides simple and easy setup, low operating temperature, low cost and environmental friendly. Therefore the author opted this method to fabricate H_2 sensor using tapered optical fiber coated with selected SMO incorporated with palladium (Pd) as a catalyst to enhance the optical responses.

In this study, the fabricated sensor is comprised of tapered multimode silica fiber (MMF) as the transducing platform. The tapering process is essential as to enhance the sensitivity to the environment through the interaction of evanescent field on the tapered surface area. The tapered region is then coated with sensing layer which is also important factors that influence the performance of the sensor. For this work, the author focused on a few kinds of SMO material well-known for their electrochromic properties which are manganese dioxide (MnO_2), zinc oxide (ZnO) and molybdenum trioxide (MoO_3), combined with Pd as the catalytic layer. The SMOs were grown via chemical bath technique and in-situ deposited onto the tapered optical fiber. The morphology of MnO_2, ZnO and MoO_3 synthesized and deposited on optical fiber were found to be nanograins, nanoflowers and nanogranules which were well distributed over the cylindrical shaped of the tapered optical fiber. The absorbance response of these sensors was characterized in terms of response and recovery times, sensitivity, repeatability and selectivity. It was discovered that the optimum thickness where the sensors of MnO_2, ZnO and MoO_3 exhibited maximum absorbance response are 300 nm, 280 nm and 250 nm respectively. It was revealed that the annealed sensor demonstrated higher sensitivity compared to as-prepared sensor. It was discovered that annealed Pd/MoO_3 coated on tapered optical fiber sensor exhibited highest absorbance increase of 3.80 when exposed to 1% H_2 at low operating temperature of 150^oC as compared to other metal oxides nanostructures. The response and recovery times recorded were 1.2 min and 3.0 min. The developed MnO_2, ZnO and MoO_3 nanostructures coated on tapered optical fiber sensor for H_2 using CBD technique are the first of its kind according to the author’s knowledge.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra
Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENDERIA HIDROGEN MENGGUNAKAN GENTIAN OPTIK TIRUS DISALUT DENGAN OKSIDA LOGAM BERSTRUKTUR NANO MELALUI TEKNIK PEMENDAPAN MANDIAN KIMIA

Oleh

NOR AKMAR BINTI MOHD YAHYA

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Dalam tesis ini, penderia hidrogen optik baru (H_2) yang berasaskan kepada nanostructures mangan dioksida (MnO_2), zink oksida (ZnO) dan molibdenum trioksida (MoO_3) yang disalut ke atas gentian optik multimodal tirus (MMF) melalui pemendapan mandi kimia (CBD) . Penggunaan H_2 sebagai bahan bakar bersih dalam pelbagai aplikasi memerlukan pengesan praktikal dan tahan lama untuk meminimumkan risiko letupan yang berkaitan dengan sifat hidrogen yang tidak menentu. Semikonduktor logam oksida (SMO) telah digunakan secara meluas selama beberapa dekad dalam tujuan sensing H_2 kerana mudah dalam fabrikasi, berkos rendah dan mempunyai kepekaan yang tinggi. SMO filem-filem nipis berstruktur nano yang digunakan sebagai lapisan penderia telah banyak dilaporkan mengenai peningkatan kepekaan mengesan disebabkan oleh permukaan kawasan yang tinggi untuk meningkatkan interaksi lapisan penderia-molekul gas. Penderia gas SMO yang sering digunapakai adalah jenis elektrik yang berasaskan perubahan konduktiviti apabila ia bertindak balas terhadap gas H_2. Walau bagaimanapun, ia mempunyai batasan tertentu seperti mudah terjejas oleh gangguan elektromagnetik (EMI) dengan itu menjejaskan tindak balas isyarat dan percikan api kecil boleh menyalakan letupan besar jika kebocoran kepekatan H_2melebihi daripada 4% dalam persekitaran. Di sisi lain, penderia optik yang masih belum diterokai dengan baik, menawarkan kelebihan dari segi saiz, ringan, tahan terhadap EMI dan tahan lama dalam persekitaran suhu tinggi. Dengan mengintegrasikan transduser optik dengan bahan SMO, ia boleh digunakan sebagai penderia gas hidrogen. Terdapat pelbagai kaedah untuk menghasilkan bahan SMO seperti pemendapan wap kimia dan fizikal, semburan gelombang radio, pemendapan elektrokimia dan penyejatan haba. Teknik ini memerlukan persediaan rumit dengan suhu operasi yang tinggi bersama-sama dengan gas pembawa semasa proses dan memerlukan substrat konduktif untuk melaksanakan prosedur. Teknik-teknik ini juga sukar untuk dilaksanakan pada gentian optik. Secara alternatif, kaedah pemendapan mandi kimia menyediakan persediaan mudah, suhu operasi yang rendah, kos rendah dan mesra alam sekitar. Oleh itu, pengarang memilih kaedah ini untuk mengesan H_2 menggunakan gentian optik tirus yang disalut dengan SMO terpilih yang digabungkan dengan palladium (Pd) sebagai pemangkin untuk meningkatkan tindak balas optik.

Dalam kajian ini, penderia yang direka terdiri daripada gentian kaca multimodal (MMF) sebagai asas transduser. Proses penirusan adalah penting untuk meningkatkan kepekaan terhadap alam sekitar melalui interaksi gelombang evanesen di kawasan permukaan tirus. Rantau tirus kemudian dilapisi dengan lapisan penderia yang juga merupakan faktor penting yang mempengaruhi prestasi penderia tersebut. Untuk karya ini, pengarang memberi tumpuan kepada beberapa jenis bahan SMO yang terkenal dengan sifat elektrokromiknya iaitu mangan dioksida (MnO_2), zink oksida (ZnO) dan molibdenum trioksida (MoO_3), digabungkan dengan Pd sebagai lapisan pemangkin. SMOs ditumbuh melalui teknik mandi kimia secara in-situ dan didepositkan atas gentian optik tirus. Morfologi MnO_2, ZnO dan MoO_3 yang disintesis dan didepositkan pada gentian optik didapati berbentuk *nanograins, nanoflowers* dan *nanogranules* yang menyelaputi dengan baik dan sekata di atas gentian optik tirus berbentuk silinder. Respon penyerapan penderia ini dicirikan dari segi masa tindak balas dan pemulihan, kepekaan, pengulangan dan selektiviti. Telah ditemui bahawa ketebalan optimum di mana sensor MnO_2, ZnO dan MoO_3 menunjukkan tindak balas penyerapan maksimum adalah 300 nm, 280 nm dan 250 nm masing-masing. Telah didedahkan bahawa penderia yang *anneal* menunjukkan kepekaan yang lebih tinggi berbanding penderia yang tidak di *anneal*. Telah didapati bahawa Pd/MoO_3 yang disalut pada penderia gentian optik tirus menunjukkan peningkatan penyerapan tertinggi sebanyak 3.80 apabila terdedah kepada 1% H_2 pada suhu operasi yang rendah iaitu 150^{o}C berbanding dengan struktur nano oksida yang lain. Masa tindak balas dan pemulihan yang direkodkan adalah 1.2 min dan 3.0 min. MnO_2, ZnO dan MoO_3 berstruktur nano yang bersalut pada penderia gentian optik tirus untuk H_2 menggunakan teknik CBD adalah yang pertama seumpamanya menurut pengetahuan pengarang.

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I certify that a Thesis Examination Committee has met on 24 July 2018 to conduct the final examination of Nor Akmar binti Mohd Yahya on her thesis entitled "Hydrogen Sensors Using Tapered Optical Fiber Coated with Metal Oxide Nanostructures Synthesized via Chemical Bath Deposition Technique" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Name of Member of Supervisory Committee: Professor Dr. Mohd Adzir bin Mahdi

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminium oxide
CBD	Chemical bath deposition
CH_4	Methane
CO_2	Carbon dioxide
CuO	Copper oxide
DI water	Deionized water
EMI	Electromagentic Interference
Fe_2O_3	Ferum oxide
H_2	Hydrogen
H_2O	Water molecules
MMF	Multimode fiber
MnO_2	Manganese oxide
MoO_3	Molybdenum oxide
Nb_2O_5	Niobium oxide
NH_3	Ammonia
NiO	Nickle oxide
Pd	Palladium
RF	Radio frequency
SiO_2	Silica oxide
SMF	Single mode fiber
SMO	Semiconducting metal oxides
SnO_2	Tin oxide
TiO_2	Titanium oxide
TIR	Total internal reflection
Vis-NIR	Visible near-infrared
Wo_3	Tungsten oxide
ZnO	Zinc oxide

CHAPTER 1

INTRODUCTION

1.1 Overview

Hydrogen (H_2) is a colourless, odourless, nontoxic, highly volatile and inflammable. The use of H_2 as a clean source of energy in various applications such as automobiles, aircraft, fuel cells, chemical industries and food processing has drawn much attention to the safety and health concerns due to its volatile properties [1]. The gas is highly flammable and burnable in air at a very wide range of 4% to 75% by volume [2]. The leaking of H_2 with high concentration mixing with oxygen can cause explosion which is a threat to environment that includes the lives of human being. The explosive reactions can be triggered by heat, spark or even sunlight. The H_2 auto-ignition temperature (spontaneous ignition in air) is reported to be at 500 ºC [3]. In order to avoid such devastated state, research and investigation on developing suitable H_2 gas sensors prior to its purpose and application has been carried out over decades.

There are four main types of hydrogen sensors which are chemiresistor, surface acousticwave, microelectronic and optical based sensors. The most common sensors widely used are electrical sensors (chemiresistor/microelectronic) due to its low cost and high sensitivity towards gases. Even so, this type of sensor is susceptible by electromagnetic interference (EMI) thus compromising the signal response. On the other hand, optical sensors using optical fiber offers other valuable characteristic such as their small size, light weight, immune to electromagnetic interference (EMI), non-inductive with low attenuation and resilient in ruggedness with high temperature environment [4]. By manipulating the core or cladding of the optical fiber, the sensing response can be monitored through absorbance, reflectance or transmission.

W. Jin et al. [5] has reviewed on the recent development for gas detection using micro/nano-engineered optical fibers such as tapered optical fibers, fiber-tip micro-cavities, hollow-cores fibers, and suspended-core fibers. They also discussed on the detection schemes which are direct absorption (evanescent wave) and photoacoustic spectroscopy that can be applied depending on the preferred sensing method. The gas sensing optical fiber based using absorbance measurement is resulted from evanescent wave that changes to its surrounding. The light propagating in the fiber core produces evanescent field which radiates at the boundary of the core into the cladding of the optical fiber. By modifying the fiber cladding and coating it with a gas sensitive layer, the evanescent field changes when the layer interacts with the gas molecules. Thus, the light in the fiber core alters its properties upon exposure to different gas concentrations [6].

One of the ways to modify the fiber cladding is to taper the optical fiber using the heat and pull technique. As of now, the research on tapered optical fiber has drawn much attention thanks to its advantages on strong evanescent wave and simplicity of production. There are various papers reported on tapered optical fiber as a sensor including strain, humidity, temperature, refractive index, chemical (liquid/gas) and biological sensors [7]–[14]. This has portrayed that tapered optical fiber has great potential to be developed in sensors application.

There are two main approaches to detect chemical substance using fiber optic. One is by measuring the intrinsic optical properties of the target/analyte (eg. refractive index) and another is by monitoring optical properties change of the fixed indicator such as sensing layer coated on the fiber optic [15]. The later approach usually incorporates with sensing layer that is sensitive to react with target/analyte. There are many type of sensing layers that are sensitive towards hydrogen gas. Organic (polymer) and inorganic materials (semiconductor metal oxides) and composite materials have been extensively studied on its electronic, chemical and optical properties. Semiconductor metal oxides (SMO) are popular to exhibit fast response, high sensitivity, long term stability, low cost and simplicity in fabrication [16]. Materials like ZnO, NiO, SnO_2, CuO, MoO_3, TiO_2, WO_3, and Fe_2O_3 are recognized to exhibit strong gas response with conductivity change [17].

Various techniques have been studied to synthesis SMO with nanostructures which offers high surface areas to promote more gas molecules-sensing layer interaction. These techniques include electrochemical deposition, sol-gel method, thermal plasma, hydrothermal, chemical bath deposition, RF sputter, chemical/physical vapor deposition and flame spray pyrolysis [2]. With development of nanostructures SMO with easy fabrication and deposition methods, it is appealing to develop a sensitive and reliable hydrogen sensor which is able to detect leakage instantly. By combining the advantages of optical fiber sensors with sensitive nanostructures sensing layer for hydrogen gas sensing application, it is an interesting research direction to be explored.

1.2 Problem Statement

Current H_2 sensors widely used is electrical based sensors. As mentioned previously, these type of sensors have major drawbacks which are vulnerable towards EMI and small sparks could ignite massive explosion if the H_2 concentration leakage is more than 4% in the environment. This could be a threat to the human lives. Meanwhile, optical fiber sensor offers features that can overcome disadvantages of electrical sensor. By integrating this optical fiber with nanostructures metal oxides, H_2 sensors can be developed. It is important to detect H_2 concentration lower of its explosive threshold limit with fast response and high sensitivity.

Apart from that, the common nanomaterial deposition for optical fiber is based on physical deposition techniques for instance sputtering, dip-coating and drop casting methods. Sputtering technique could provide uniform coating but not quite suitable for cylindrical shape of optical fiber that could yield different thickness at certain area. Same goes with dip-coating and drop casting methods with easy techniques but hardly produce controlled thickness and the sensing layer attachment on optical fiber is poor. On the contrary, chemical bath deposition (CBD) method could offer better solution for sensing layer coating problem. This technique exhibits homogenous and uniform coating towards cylindrical shape of optical fiber as well as controlled thickness. Furthermore, the sensing layer coating is chemically bonded which makes the adherent strong. This technique is also simple and easy to perform. To coat SMO on optical fiber using CBD technique is still not establish. Therefore, different SMO are required to produce high viability for optical fiber coating.

1.3 Objectives

This thesis focuses on the development of tapered optical fiber sensors coated with metal oxide nanostructures for H_2 sensing application via chemical bath deposition. The objectives of this research are as follows:

- To design and develop hydrogen gas sensors based on metal oxides nanostructures coated on tapered optical fiber via chemical bath deposition method.
- To micro-characterize the synthesized metal oxides nanostructures.
- To evaluate the optical fiber sensor performance (sensitivity, response & recovery time, repeatability, and selectivity) based on absorbance measurement.
- To discuss the sensing mechanism of gas molecules-sensing layer interaction of tapered optical fiber sensor.

In order to achieve these goals, the following research questions are outlined accordingly:

- What are the semiconductor metal oxides that are sensitive and change its optical properties when interact with H_2 gas?
- How these materials can be synthesized and coated onto tapered optical fiber?
- Which optical measurement can be used to investigate the response of the developed sensors toward H_2 gas?
- How different are the sensing performance with different waist diameter of tapered optical fiber?
- How different are the sensing performance of semiconductor metal oxides with different thicknesses and morphologies?

With these research questions, the investigation focused on a few type of semiconductor metal oxides (SMO) which are known for their sensing properties towards H_2 gas. In addition to that, nanostructured SMO has the ability to produce outstanding gasochromic properties as suggested in literature review. Based on the above reference, the author has developed optical fiber sensors based on manganese dioxide (MnO_2), zinc oxide (ZnO) and molybdenum trioxide (MoO_3) nanostructures incorporate with nobel metal catalyst of palladium (Pd). The nanostructures of these SMO were synthesized and deposited via chemical bath depositon (CBD) technique onto tapered optical fiber which was then coated with very thin layer of Pd (5nm). To the best of the author's knowledge, none of these SMO synthesized via CBD coated on tapered multimode optical fiber for H_2 detection have been reported or published. The optical responses were analysed in term of their gas sensing performance and micro-characterization that has helped the author to understand more on the gas interaction mechanism in optical sensors. The description of the research project is illustrated in Figure 1.1.

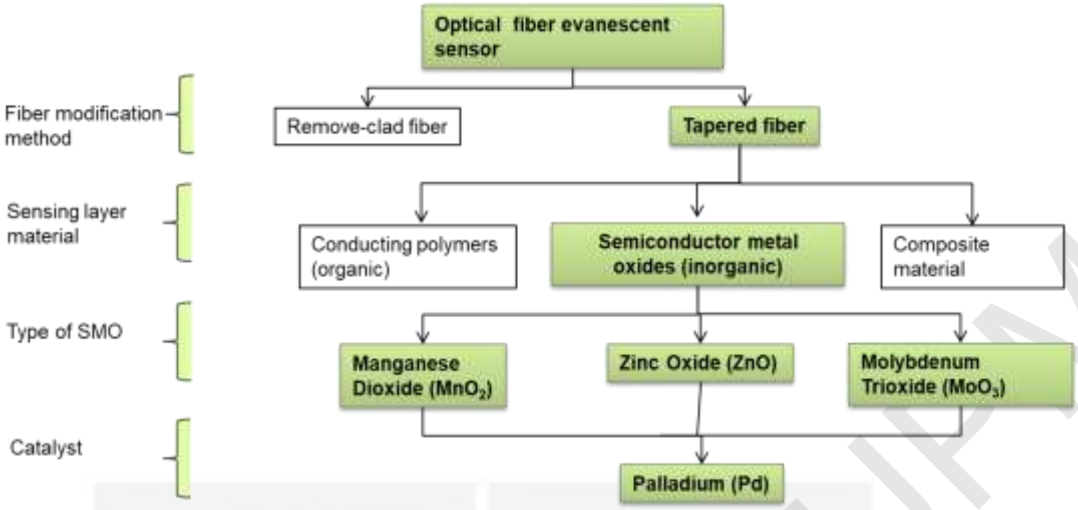

Figure 1.1 : Research design of the project

1.4 Scope of Work and Limitation

In this research project, the author focuses on the synthesis of selected SMO via chemical bath deposition technique onto tapered optical fiber. The dimension profile of waist length is fixed to 10 mm and the up/down taper is 2 mm. This profile is well-establised and adequate to provide sensitivity suitable for gas sensing and easy to handle [18]. The deposition parameters are varied to study on the thicknesses and morphologies of the sensing layer. The as-prepared and anneal sensors were prepared to test on their H_2 sensing performance. The investigation was further discussed on the effect of with/without Pd catalyst towards sensing response. The optimum operating temperature for H_2 sensing was also tested so the largest response can be obtained. Sensitivity and repeatability of the fabricated sensors were determined as well as selectivity towards other gases was also measured. Throughout this project, a very thin layer of palladium is DC sputtered on top of the sensing layer. Although the research work focuses on chemical deposition method of SMO that offers better coating and adherent, DC sputtering is used for Pd due to its function is solely as a catalyst and only complementing the actual sensing layer.

1.5 Thesis Organisation

This thesis consists of 6 chapters. Chapter 1 basically touches on the overview of the research work, problem statements, objective and thesis outline. The background of previous works and literature reviews related to the project were discussed and presented in Chapter 2. Methods of developing and fabricating the sensors including how tapered optical fiber was produced as well as SMO synthesization and deposition techniques via chemical bath were clarified in Chapter 3. Description on equipment used for micro-characterization measurement plus gas sensing setup and measurement were reviewed in Chapter 4. Chapter 5 mainly discusses on the results of each of the sensing layer of SMO sensors fabricated in terms of its micro-characterization and sensing response towards H_2 gas. Finally, Chapter 6 concludes all the work done and summarises some future research suggestion.

REFERENCES

[1] I. H. Kadhim, H. Abu Hassan, and Q. N. Abdullah, “Hydrogen gas sensor based on nanocrystalline SnO2 Thin Film grown on bare Si substrates,” *Nano-Micro Lett.*, vol. 8, no. 1, pp. 20–28, 2016.

[2] W. Chomkitichai, H. Ninsonthi, C. Liewhiran, A. Wisitsoraat, S. Sriwichai, and S. Phanichphant, “Flame-Made Pt-Loaded TiO 2 Thin Films and Their Application as H 2 Gas Sensors,” vol. 2013, 2013.

[3] P. Patnaik, *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*. 2007.

[4] B. Lee, “Review of the present status of optical fiber sensors,” vol. 9, pp. 57–79, 2003.

[5] W. Jin, H. L. Ho, Y. C. Cao, J. Ju, and L. F. Qi, “Optical Fiber Technology Gas detection with micro- and nano-engineered optical fibers q,” vol. 19, pp. 741–759, 2013.

[6] N. A. M. Yahya, M. R. Y. Hamid, S. A. Ibrahim, B. H. Ong, N. A. Rahman, A. R. M. Zain, M. A. Mahdi, and M. H. Yaacob, “H 2 sensor based on tapered optical fiber coated with MnO 2 nanostructures,” *Sensors Actuators B Chem.*, vol. 246, pp. 421–427, 2017.

[7] J. M. Corres, F. J. Arregui, A. Member, I. R. Matias, and S. Member, “Design of Humidity Sensors Based on Tapered Optical Fibers,” vol. 24, no. 11, pp. 4329–4336, 2006.

[8] Z. Yu, L. Jin, L. Sun, J. Li, Y. Ran, and B. O. Guan, “Highly Sensitive Fiber Taper Interferometric Hydrogen Sensors,” *IEEE Photonics J.*, vol. 8, no. 1, 2016.

[9] M. Irigoyen, J. A. Sánchez-Martin, E. Bernabeu, and A. Zamora, “Tapered optical fiber sensor for chemical pollutants detection in seawater,” *Meas. Sci. Technol.*, vol. 28, no. 4, p. 45802, 2017.

[10] H. Latifi, M. I. Zibaii, S. M. Hosseini, and P. Jorge, “Nonadiabatic tapered optical fiber for biosensor applications,” *Photonic Sensors*, vol. 2, no. 4, pp. 340–356, 2012.

[11] H. F. Lima, P. F. Antunes, J. De Lemos Pinto, and R. N. Nogueira, “Simultaneous measurement of strain and temperature with a single fiber Bragg grating written in a tapered optical fiber,” *IEEE Sens. J.*, vol. 10, no. 2, pp. 269–273, 2010.

[12] Y. Tian, W. Wang, N. Wu, X. Zou, and X. Wang, “Tapered optical fiber sensor for label-free detection of biomolecules,” *Sensors*, vol. 11, no. 4, pp. 3780–3790, 2011.

[13] M. Lo, “Tapered optical-fiber-based pressure sensor,” pp. 2241–2247, 2013.

[14] S. Zhu, F. Pang, and T. Wang, “Single-mode tapered optical fiber for temperature sensor based on multimode interference,” vol. 8311, p. 83112B, 2011.

[15] N. Xue, Q. Zhang, S. Zhang, P. Zong, and F. Yang, “Highly Sensitive and Selective Hydrogen Gas Sensor Using the Mesoporous SnO2 Modified Layers,” *Sensors*, vol. 17, no. 10, p. 2351, 2017.

[16] H. Gu, Z. Wang, and Y. Hu, *Hydrogen Gas Sensors Based on Semiconductor Oxide Nanostructures*, vol. 12, no. 12. 2012.

[17] C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, “Metal oxide gas sensors: sensitivity and influencing factors.,” *Sensors (Basel).*, vol. 10, no. 3, pp. 2088–106, Jan. 2010.

[18] S. A. Ibrahim, “FEASIBILITY STUDIES OF POLYANILINE NANOSTRUCTURES COATED ON TAPERED OPTICAL FIBER FOR AMMONIA SENSING By SITI AZLIDA BINTI IBRAHIM @ GHAZALI,” no. January, 2017.

[19] “Fiber Optics Communication.” [Online]. Available: http://www.iasscore.in/upsc-prelims/fiber-optic-communication.

[20] B&W Tek, “No Title,” 2017. [Online]. Available: http://bwtek.com/spectrometer-part-6-choosing-a-fiber-optic/.

[21] B. Renganathan, D. Sastikumar, G. Gobi, N. R. Yogamalar, and A. C. Bose, “Optics & Laser Technology Nanocrystalline ZnO coated fiber optic sensor for ammonia gas detection,” *Opt. Laser Technol.*, vol. 43, no. 8, pp. 1398–1404, 2011.

[22] M. H. Yaacob, “Investigation of Metal Oxide Nanostructured Thin Films Based Optical Hydrogen Sensors,” no. March, 2012.

[23] S. Ko, J. Lee, J. Koo, B. S. Joo, M. Gu, and J. H. Lee, “Chemical wet etching of an optical fiber using a hydrogen fluoride-free solution for a saturable absorber based on the evanescent field interaction,” *J. Light. Technol.*, vol. 34, no. 16, pp. 3776–3784, 2016.

[24] X. Chong, K. J. Kim, P. R. Ohodnicki, E. Li, C. H. Chang, and A. X. Wang, “Ultrashort Near-Infrared Fiber-Optic Sensors for Carbon Dioxide Detection,” *IEEE Sens. J.*, vol. 15, no. 9, pp. 5327–5332, 2015.

[25] Y.-T. Luo, H.-B. Wang, G.-M. Ma, H.-T. Song, C. Li, and J. Jiang, “Research on High Sensitive D-Shaped FBG Hydrogen Sensors in Power Transformer Oil,” *Sensors*, vol. 16, no. 10, p. 1641, 2016.

[26] J. D. Gordon, “Using and Optical D-FIber as a chemical sensor,” no. April, 2007.

[27] J. Dai, M. Yang, Y. Chen, K. Cao, H. Liao, and P. Zhang, "Side-polished fiber Bragg grating hydrogen sensor with WO_3-Pd composite film as sensing materials," *Opt. Express*, vol. 19, no. 7, p. 6141, 2011.

[28] M. R. R. Khan and S. W. Kang, "A high sensitivity and wide dynamic range fiber-optic sensor for low-concentration VOC gas detection," *Sensors (Switzerland)*, vol. 14, no. 12, pp. 23321–23336, 2014.

[29] W. Jin, H. L. Ho, Y. C. Cao, J. Ju, and L. F. Qi, "Optical Fiber Technology Gas detection with micro- and nano-engineered optical fibers q," vol. 19, pp. 741–759, 2013.

[30] B. Lee, S. Roh, and J. Park, "Current status of micro- and nano-structured optical fiber sensors," *Opt. Fiber Technol.*, vol. 15, no. 3, pp. 209–221, Jun. 2009.

[31] G. Brambilla, V. Finazzi, and D. Richardson, "Ultra-low-loss optical fiber nanotapers," *Opt. Express*, vol. 12, no. 10, pp. 2258–2263, 2004.

[32] W. Bin Ji, H. H. Liu, S. C. Tjin, K. K. Chow, and A. Lim, "Ultrahigh Sensitivity Refractive Index Sensor Based on Optical Microfiber," vol. 24, no. 20, pp. 1872–1874, 2012.

[33] N. E. González-Sierra, L. del C. Gómez-Pavón, G. F. Pérez-Sánchez, A. Luis-Ramos, P. Zaca-Morán, J. M. Muñoz-Pacheco, and F. Chávez-Ramírez, "Tapered optical fiber functionalized with palladium nanoparticles by drop casting and laser radiation for H2and volatile organic compounds sensing purposes," *Sensors (Switzerland)*, vol. 17, no. 9, 2017.

[34] S. Svanberg, *Atomic and Molecular Spectroscopy*. Springer-Verlag Berlin Heidelberg, 2004.

[35] E. H. Korteb, "IR Specular Reflectance Studies on Rough-Sudan Solids and on Layered Systems with Nonuniform Interfaces: Optical Simulations," vol. 293, pp. 245–248, 1993.

[36] S. Basu and P. K. Basu, "Nanocrystalline metal oxides for methane sensors: Role of noble metals," *J. Sensors*, vol. 2009, 2009.

[37] P. Shankar, J. Bosco, and B. Rayappan, "Gas sensing mechanism of metal oxides : The role of ambient atmosphere , type of semiconductor and gases - A review ScienceJet," *Sci. Jet*, vol. 4, no. JANUARY 2015, p. 126, 2015.

[38] M. H. Yaacob, J. Yu, K. Latham, K. Kalantar-Zadeh, and W. Wlodarski, "Optical hydrogen sensing properties of nanostructured Pd/MoO3 films," *Sens. Lett.*, vol. 9, no. 1, pp. 16–20, 2011.

[39] H. Koyanaka, Y. Ueda, K. Takeuchi, and A. I. Kolesnikov, “Effect of crystal structure of manganese dioxide on response for electrolyte of a hydrogen sensor operative at room temperature,” *Sensors Actuators B Chem.*, vol. 183, pp. 641–647, Jul. 2013.

[40] A. Sanger, A. Kumar, A. Kumar, and R. Chandra, “Highly sensitive and selective hydrogen gas sensor using sputtered grown Pd decorated MnO2 nanowalls,” *Sensors Actuators B Chem.*, vol. 234, pp. 8–14, 2016.

[41] M. Angiola, M. M. Y. A. Alsaif, K. Kalantar-Zadeh, A. Wisitsoraat, W. Wlodarski, and A. Martucci, “Optical hydrogen sensing based on hybrid 2D MoO3/Au nanoparticles,” *Procedia Eng.*, vol. 120, pp. 1141–1144, 2015.

[42] S. Ozturk, N. Kilinc, and Z. Z. Ozturk, “The effects of annealing on gas sensing properties of ZnO nanorod sensors coated with Pd and Pt,” *Procedia Eng.*, vol. 47, pp. 434–437, 2012.

[43] L. Rajan, C. Periasamy, and V. Sahula, “Comprehensive Study on Electrical and Hydrogen Gas Sensing Characteristics of Pt/ZnO Thin Film Based Schottky Diodes Grown on n-Si Substrates by RF sputtering,” *IEEE Trans. Nanotechnol.*, vol. PP, no. 99, pp. 1–1, 2016.

[44] S. Phanichphant, “Semiconductor Metal Oxides as Hydrogen Gas Sensors,” *Procedia Eng.*, vol. 87, pp. 795–802, 2014.

[45] J. A. Rodriguez, T. Jirsak, and S. Chaturvedi, “Reaction of H2S with MgO(100) and Cu/MgO(100) surfaces: Band-gap size and chemical reactivity,” *J. Chem. Phys.*, vol. 111, no. 17, pp. 8077–8087, 1999.

[46] R. M. Pasquarelli, D. S. Ginley, and R. O’Hayre, “Solution processing of transparent conductors: From flask to film,” *Chem. Soc. Rev.*, vol. 40, no. 11, pp. 5406–5441, 2011.

[47] C. Kittel and H. Y. Fan, “Introduction to Solid State Physics,” *Am. J. Phys.*, vol. 25, no. 5, pp. 330–330, 1957.

[48] Q. P. Zhang, X. N. Xu, Y. T. Liu, M. Xu, S. H. Deng, Y. Chen, H. Yuan, F. Yu, Y. Huang, K. Zhao, S. Xu, and G. Xiong, “A feasible strategy to balance the crystallinity and specific surface area of metal oxide nanocrystals,” *Sci. Rep.*, vol. 7, pp. 1–12, 2017.

[49] S. Pati, S. B. Majumder, and P. Banerji, “Role of oxygen vacancy in optical and gas sensing characteristics of ZnO thin films,” *J. Alloys Compd.*, vol. 541, pp. 376–379, 2012.

[50] R. Kumar, O. Al-Dossary, G. Kumar, and A. Umar, “Zinc oxide nanostructures for NO2 gas–sensor applications: A review,” *Nano-Micro Lett.*, vol. 7, no. 2, pp. 97–120, 2015.

[51] J. Lv, W. Gong, K. Huang, J. Zhu, F. Meng, X. Song, and Z. Sun, “Ww W M . Ww W M .,” vol. 50, pp. 98–106, 2011.

[52] K. A. M. Ahmed, “Exploitation of KMnO4 material as precursors for the fabrication of manganese oxide nanomaterials,” *J. Taibah Univ. Sci.*, Aug. 2015.

[53] M. A. Haque and S. Mahalakshmi, “Effect of Annealing on Structure and Morphology of Cadmium Sulphide Thin Film Prepared by Chemical Bath Deposition,” *J. Adv. Phys.*, vol. 3, no. 2, pp. 159–162, 2014.

[54] A. Dhara, G. Hodes, and S. K. Sarkar, “Two stage chemical bath deposition of MoO3 nanorod films,” *RSC Adv.*, vol. 4, no. 96, pp. 53694–53700, 2014.

[55] M. Kokotov and G. Hodes, “Reliable chemical bath deposition of ZnO films with controllable morphology from ethanolamine-based solutions using KMnO4 substrate activation,” *J. Mater. Chem.*, vol. 19, no. 23, p. 3847, 2009.

[56] R. H. Bari and S. B. Patil, “Studies on Spray Pyrolised Nanostructured SnO2 Thin Films for H2 Gas Sensing Application,” *Int. Lett. Chem. Phys. Astron.*, vol. 36, pp. 125–141, 2014.

[57] G. Gasparotto, T. Mazon, G. Gasparotto, M. A. Zaghete, L. A. Perazolli, and J. A. Varela, “Gas Sensor Properties of ZnO Nanorods Grown by Chemical Bath Deposition,” *Adv. Mater. Res.*, vol. 975, pp. 189–193, 2014.

[58] N. Banerjee, S. Roy, C. K. Sarkar, and S. Member, “Pd Modified ZnO Nanorod based High Dynamic Range Hydrogen Sensor,” pp. 682–685, 2013.

[59] M. B. Rahmani, S. H. Keshmiri, J. Yu, A. Z. Sadek, L. Al-Mashat, A. Moafi, K. Latham, Y. X. Li, W. Wlodarski, and K. Kalantar-zadeh, “Gas sensing properties of thermally evaporated lamellar MoO3,” *Sensors Actuators, B Chem.*, vol. 145, no. 1, pp. 13–19, 2010.

[60] G. Korotcenkov, “Metal oxides for solid-state gas sensors : What determines our choice ?,” vol. 139, pp. 1–23, 2007.

[61] M. H. Yaacob, M. Breedon, and W. Wlodarski, “Sensors and Actuators B : Chemical Absorption spectral response of nanotextured WO 3 thin films with Pt catalyst towards H 2 ଝ,” vol. 137, pp. 115–120, 2009.

[62] J. Ou, M. H. Yaacob, J. L. Campbell, K. Kalantar-zadeh, and W. Wlodarski, “H2 sensing performance of optical fiber coated with nano-platelet WO3 film,” *Procedia Eng.*, vol. 5, pp. 1204–1207, 2010.

[63] P. R. Ohodnicki, M. Andio, and C. Wang, “Optical gas sensing responses in transparent conducting oxides with large free carrier density,” *J. Appl. Phys.*, vol. 116, no. 2, 2014.

[64] Q. Yan, S. Tao, and H. Toghiani, “Optical fiber evanescent wave absorption spectrometry of nanocrystalline tin oxide thin films for selective hydrogen sensing in high temperature gas samples.,” *Talanta*, vol. 77, no. 3, pp. 953–61, Jan. 2009.

[65] S. Pishdadian and a. M. Shariati Ghaleno, “Influences of Annealing Temperature on the Optical and Structural Properties of Manganese Oxide Thin Film by Zn Doping from Sol-Gel Technique,” *Acta Phys. Pol. A*, vol. 123, no. 4, pp. 741–745, Apr. 2013.

[66] M. Wang and Y. Feng, “Palladium-silver thin film for hydrogen sensing,” *Sensors Actuators, B Chem.*, vol. 123, no. 1, pp. 101–106, 2007.

[67] H. and K. O. Feng, Q., Kanoh, “Manganese Oxide Porous Crystal,” *J. Mater*, vol. 9, pp. 319–33, 1999.

[68] B. Renganathan and A. R. Ganesan, “Optical Fiber Technology Fiber optic gas sensor with nanocrystalline ZnO,” *Opt. Fiber Technol.*, vol. 20, no. 1, pp. 48–52, 2014.

[69] A. A. Hendi and R. H. Alorainy, “New fabrication of zinc oxide nanostructure thin film gas sensors,” *Superlattices Microstruct.*, vol. 66, pp. 23–32, 2014.

[70] R. Wahab, F. Khan, N. Ahmad, H.-S. Shin, J. Musarrat, and A. A. Al-Khedhairy, “Hydrogen adsorption properties of nano- and microstructures of ZnO,” *J. Nanomater.*, vol. 2013, 2013.

[71] S. Roy, H. Saha, and C. K. Sarkar, “HIGH SENSITIVITY METHANE SENSOR BY CHEMICALLY,” vol. 3, no. 4, pp. 605–620, 2010.

[72] D. E. Motaung, G. H. Mhlongo, I. Kortidis, S. S. Nkosi, G. F. Malgas, B. W. Mwakikunga, S. S. Ray, and G. Kiriakidis, “Structural and optical properties of ZnO nanostructures grown by aerosol spray pyrolysis: Candidates for room temperature methane and hydrogen gas sensing,” *Appl. Surf. Sci.*, vol. 279, pp. 142–149, 2013.

[73] S. N. Das, J. P. Kar, J.-H. Choi, T. Il Lee, K.-J. Moon, and J.-M. Myoung, “Fabrication and Characterization of ZnO Single Nanowire-Based Hydrogen Sensor,” *J. Phys. Chem. C*, vol. 114, no. 3, pp. 1689–1693, 2010.

[74] H. T. Wang, B. S. Kang, F. Ren, L. C. Tien, P. W. Sadik, D. P. Norton, S. J. Pearton, and J. Lin, “Detection of hydrogen at room temperature with catalyst-coated multiple ZnO nanorods,” *Appl. Phys. A Mater. Sci. Process.*, vol. 81, no. 6, pp. 1117–1119, 2005.

[75] P. Pimpang, A. S. Zoolfakar, R. A. Rani, R. A. Kadir, D. Wongratanaphisan, A. Gardchareon, K. Kalantar-zadeh, and S. Choopun, “Hydrogen sensors based on gold nanoclusters assembled onto ZnO nanostructures at low operating temperature,” *Ceram. Int.*, vol. 43, pp. S511–S515, 2017.

[76] A. O. Dikovska, G. B. Atanasova, N. N. Nedyalkov, P. K. Stefanov, P. A. Atanasov, E. I. Karakoleva, and A. T. Andreev, “Optical sensing of ammonia using ZnO nanostructure grown on a side-polished optical-fiber,” *Sensors Actuators, B Chem.*, vol. 146, no. 1, pp. 331–336, 2010.

[77] R. Tabassum and B. D. Gupta, “Surface plasmon resonance-based fiber-optic hydrogen gas sensor utilizing palladium supported zinc oxide multilayers and their nanocomposite,” *Appl. Opt.*, vol. 54, no. 5, p. 1032, 2015.

[78] A. Chithambararaj, N. Rajeswari Yogamalar, and A. C. Bose, “Hydrothermally Synthesized h-MoO $_3$ and α-MoO $_3$ Nanocrystals: New Findings on Crystal-Structure-Dependent Charge Transport,” *Cryst. Growth Des.*, vol. 16, no. 4, pp. 1984–1995, 2016.

[79] J. Zhou, N. Lin, L. Wang, K. Zhang, Y. Zhu, and Y. Qian, “Synthesis of hexagonal MoO $_3$ nanorods and a study of their electrochemical performance as anode materials for lithium-ion batteries,” *J. Mater. Chem. A*, vol. 3, no. 14, pp. 7463–7468, 2015.

[80] A. Chithambararaj, N. S. Sanjini, S. Velmathi, and A. Chandra Bose, “Preparation of h-MoO3 and α-MoO3 nanocrystals: comparative study on photocatalytic degradation of methylene blue under visible light irradiation,” *Phys. Chem. Chem. Phys.*, vol. 15, no. 35, p. 14761, 2013.

[81] Y. Xu, L. Xie, Y. Zhang, and X. Cao, “Hydrothermal synthesis of hexagonal MoO3 and its reversible electrochemical behavior as a cathode for Li-ion batteries,” *Electron. Mater. Lett.*, vol. 9, no. 5, pp. 693–696, 2013.

[82] J. Song, X. Ni, L. Gao, and H. Zheng, “Synthesis of metastable h-MoO3 by simple chemical precipitation,” *Mater. Chem. Phys.*, vol. 102, no. 2–3, pp. 245–248, 2007.

[83] N. Illyaskutty, H. Kohler, T. Trautmann, M. Schwotzer, and V. P. Mahadevan Pillai, “Hydrogen and ethanol sensing properties of molybdenum oxide nanorods based thin films: Effect of electrode metallization and humid ambience,” *Sensors Actuators, B Chem.*, vol. 187, pp. 611–621, 2013.

[84] H. Shanak, H. Schmitt, J. Nowoczin, and C. Ziebert, “Effect of Pt-catalyst on gasochromic WO3 films: Optical, electrical and AFM investigations,” *Solid State Ionics*, vol. 171, no. 1–2, pp. 99–106, 2004.

[85] J. S. Noh, J. M. Lee, and W. Lee, “Low-dimensional palladium nanostructures for fast and reliable hydrogen gas detection,” *Sensors*, vol. 11, no. 1, pp. 825–851, 2011.

[86] B. D. Adams and A. Chen, “The role of palladium in a hydrogen economy,” *Mater. Today*, vol. 14, no. 6, pp. 282–289, 2011.

[87] F. D. Manchester, A. San-Martin, and J. M. Pitre, “The H-Pd (hydrogen-palladium) System,” *J. Phase Equilibria*, vol. 15, no. 1, pp. 62–83, 1994.

[88] P. Soundarrajan and F. Schweighardt, “Hydrogen Sensing and Detection,” 2009.

[89] J. Villatoro, D. Luna-Moreno, and D. Monzón-Hernández, “Optical fiber hydrogen sensor for concentrations below the lower explosive limit,” *Sensors Actuators, B Chem.*, vol. 110, no. 1, pp. 23–27, 2005.

[90] A. B. Socorro, I. Del Villar, J. M. Corres, I. R. Matias, and F. J. Arregui, “Lossy mode resonances dependence on the geometry of a tapered monomode optical fiber,” *Sensors Actuators, A Phys.*, vol. 180, pp. 25–31, 2012.

[91] S. A. Ibrahim, N. A. Rahman, M. H. Abu Bakar, S. H. Girei, M. H. Yaacob, H. Ahmad, and M. A. Mahdi, “Room temperature ammonia sensing using tapered multimode fiber coated with polyaniline nanofibers,” *Opt. Express*, vol. 23, no. 3, p. 2837, 2015.

[92] L. F. Koao, F. B. Dejene, and H. C. Swart, “Synthesis of pbs nanostructures by chemical bath deposition method,” *Int. J. Electrochem. Sci.*, vol. 9, no. 4, pp. 1747–1757, 2014.

[93] N. R. Chodankar, G. S. Gund, D. P. Dubal, and C. D. Lokhande, “Alcohol mediated growth of α-MnO 2 thin films from KMnO 4 precursor for high performance supercapacitors,” *RSC Adv.*, vol. 4, no. 106, pp. 61503–61513, Nov. 2014.

[94] W. Song, “Growth and Characterization of Zn x Cd 1 x S Films Prepared by Using Chemical Bath Deposition for Photovoltaic Devices,” vol. 54, no. 4, pp. 1660–1665, 2009.

[95] C. D. Lokhande, E. H. Lee, K. D. Jung, and O. S. Joo, “Ammonia-free chemical bath method for deposition of microcrystalline cadmium selenide films,” *Mater. Chem. Phys.*, vol. 91, no. 1, pp. 200–204, 2005.

[96] N. Rathore, D. V. S. Rao, and S. K. Sarkar, “Growth of a polarity controlled ZnO nanorod array on a glass/FTO substrate by chemical bath deposition,” *RSC Adv.*, vol. 5, no. 36, pp. 28251–28257, 2015.

[97] G.-J. Janssen, “Information on the FESEM (Field-emission Scanning Electron Microscope),” *Radboud Univ. Nijmegen*, pp. 1–5, 2015.

[98] University of California, “Introduction to Energy Dispersive X-ray Spectrometry (EDS),” pp. 1–12, 2015.

[99] T. A. X. Company, “The multi-purpose solution for your analytical needs The Analytical X-ray Company Pioneering X-ray diffraction,” pp. 1–20, 2000.

[100] T. Thermogravimetric and I. Family, “Thermogravimetric Analysis (TGA) A Beginner â€™ s Guide,” 1960.

[101] B. D. Viezbicke, S. Patel, B. E. Davis, and D. P. Birnie, “Evaluation of the Tauc method for optical absorption edge determination: ZnO thin films as a model system,” *Phys. Status Solidi*, vol. 252, no. 8, pp. 1700–1710, 2015.

[102] B. F. Kalantar-Zadeh, Kourosh, *Nanotechnology-Enabled Sensor*. Springer US, 2008.

[103] V. E. Bochenkov and G. B. Sergeev, “Sensitivity , Selectivity , and Stability of Gas-Sensitive Metal-Oxide Nanostructures,” vol. 3, pp. 31–52, 2010.

[104] A. Aziz, H. N. Lim, S. H. Girei, M. H. Yaacob, M. A. Mahdi, N. M. Huang, and A. Pandikumar, “Sensors and Actuators B : Chemical Silver / graphene nanocomposite-modified optical fiber sensor platform for ethanol detection in water medium,” *Sensors Actuators B. Chem.*, vol. 206, pp. 119–125, 2015.

[105] I. Jiménez, J. Arbiol, G. Dezanneau, A. Cornet, and J. R. Morante, “Crystalline structure, defects and gas sensor response to NO2 and H2S of tungsten trioxide nanopowders,” *Sensors Actuators, B Chem.*, vol. 93, no. 1–3, pp. 475–485, 2003.

[106] C. Julien, M. Massot, S. Rangan, M. Lemal, and D. Guyomard, “Study of structural defects in ??-MnO2 by Raman spectroscopy,” *J. Raman Spectrosc.*, vol. 33, no. 4, pp. 223–228, 2002.

[107] S. M. Baschenko and L. S. Marchenko, “On Raman spectra of water , its structure and dependence on temperature,” *Semicond. Physics, Quantum Electron. Optoelectron.*, vol. 14, no. 1, pp. 77–79, 2011.

[108] Y. Hu, H. Zhu, J. Wang, and Z. Chen, “Synthesis of layered birnessite-type manganese oxide thin films on plastic substrates by chemical bath deposition for flexible transparent supercapacitors,” *J. Alloys Compd.*, vol. 509, no. 42, pp. 10234–10240, 2011.

[109] N. Rajamanickam, P. Ganesan, S. Rajashabala, and K. Ramachandran, “Structural and optical properties of ??-MnO2 nanowires and ??- MnO2 nanorods,” *AIP Conf. Proc.*, vol. 1591, pp. 267–269, 2014.

[110] N. Minh, H. Nhat, H. Yi, D. Kim, Y. Han, and M. Kim, “Sensors and Actuators B : Chemical Ni 2 O 3 -decorated SnO 2 particulate films for methane gas sensors,” *Sensors Actuators B. Chem.*, vol. 192, pp. 327–333, 2014.

[111] Y. Zhang, L. Zhang, J. Deng, S. Xie, and H. Yang, “Synthesis , Characterization , and Catalytic Properties of MnO x / SBA-16 for Toluene Oxidation,” pp. 154–167.

[112] H. Shanak and H. Schmitt, “Fast coloration in sputtered gasochromic tungsten oxide films,” *Phys. Status Solidi Appl. Mater. Sci.*, vol. 203, no. 15, pp. 3748–3753, 2006.

[113] J. Z. Ou, M. H. Yaacob, J. L. Campbell, M. Breedon, K. Kalantar-zadeh, and W. Wlodarski, “Sensors and Actuators B : Chemical H 2 sensing performance of optical fiber coated with nano-platelet WO 3 film ଝ,” vol. 167, pp. 1–6, 2012.

[114] J. Z. Ou, M. H. Yaacob, M. Breedon, H. D. Zheng, J. L. Campbell, K. Latham, J. du. Plessis, W. Wlodarski, and K. Kalantar-zadeh, “In situ Raman spectroscopy of H2 interaction with WO3 films,” *Phys. Chem. Chem. Phys.*, vol. 13, no. 16, p. 7330, 2011.

[115] M. H. Yaacob, A. Z. Sadek, K. Latham, K. Kalantar-zadeh, and W. Wlodarski, “Procedia Chemistry Optical H 2 Sensing Performance of Anodized Nanoporous TiO 2 Thin Films,” *PROCHE*, vol. 1, no. 1, pp. 951–954, 2009.

[116] S. M. Kim, H. Lee, and J. Y. Park, “Charge Transport in Metal???Oxide Interfaces: Genesis and Detection of Hot Electron Flow and Its Role in Heterogeneous Catalysis,” *Catal. Letters*, pp. 299–308, 2014.

[117] S. Bai, T. Guo, D. Li, R. Luo, A. Chen, and C. C. Liu, “Intrinsic sensing properties of the flower-like ZnO nanostructures,” *Sensors Actuators, B Chem.*, vol. 182, pp. 747–754, 2013.

[118] R. Zhang, P. G. Yin, N. Wang, and L. Guo, “Photoluminescence and Raman scattering of ZnO nanorods,” *Solid State Sci.*, vol. 11, no. 4, pp. 865–869, 2009.

[119] R. P. Wang, G. Xu, and P. Jin, “Size dependence of electron-phonon coupling in ZnO nanowires,” *Phys. Rev. B*, vol. 69, no. 11, p. 113303, 2004.

[120] A. H. Moharram, S. A. Mansour, M. A. Hussein, and M. Rashad, “Direct precipitation and characterization of ZnO nanoparticles,” *J. Nanomater.*, vol. 2014, 2014.

[121] I. U. Abhulimen, X. B. Chen, J. L. Morrison, V. K. Rangari, L. Bergman, K. Das, S. Bagheri, K. G. Chandrappa, S. B. A. Hamid, I. E. Characterization, C. References, M. I. Khalil, M. M. Al-Qunaibit, A. M. Al-zahem, J. P. Labis, A. Kołodziejczak-Radzimska, T. Jesionowski, M. Thirumavalavan, K.-L. Huang, and J.-F. Lee, “Synthesis and characterization of ZnO nanoparticles by thermal decomposition of a curcumin zinc complex,” *Materials (Basel).*, vol. 7, no. 3, pp. 4198–4212, 2013.

[122] V. Srikant and D. R. Clarke, “On the optical band gap of zinc oxide,” *J. Appl. Phys.*, vol. 83, no. 10, pp. 5447–5451, 1998.

[123] G. Tang, H. Liu, and W. Zhang, “The variation of optical band gap for ZnO:In films prepared by sol-gel technique,” *Adv. Mater. Sci. Eng.*, vol. 2013, pp. 1–5, 2013.

[124] C. H. Tan, S. T. Tan, H. B. Lee, C. C. Yap, and M. Yahaya, “Growth concentration effect on oxygen vacancy induced band gap narrowing and optical CO gas sensing properties of ZnO nanorods,” *AIP Conf. Proc.*, vol. 1784, 2016.

[125] S. Di and M. Falasconi, “Drift Correction Methods for Gas Chemical Sensors in Artificial Olfaction Systems: Techniques and Challenges,” *Adv. Chem. Sensors*, pp. 305–326, 2012.

[126] A. Arasu and V. Williams, “Effect of Annealing Temperature on the Dispersion Energy Parameters of Sol-Gel Routed Molybdenum Oxide Thin Film,” vol. 22, no. 4, pp. 1–8, 2015.

[127] G. Huyberechts and P. Szeco, “Simultaneous quantification of carbon monoxide and methane in humid air using a sensor array and an artificial neural network,” vol. 45, pp. 123–130, 1997.

[128] Y. Li, H. Yu, X. Huang, Z. Wu, and M. Chen, “A simple synthesis method to prepare a molybdenum oxide hole-transporting layer for efficient polymer solar cells,” *RSC Adv.*, vol. 7, no. 13, pp. 7890–7900, 2017.

[129] A. Chithambararaj and A. C. Bose, “Hydrothermal synthesis of molybdenum oxide microbelts,” *AIP Conf. Proc.*, vol. 1447, no. 1, pp. 311–312, 2012.

[130] V. A. Doss, A. Chithambararaj, and A. C. Bose, “Effect of reaction atmosphere on structural and optical properties of hexagonal molybdenum oxide (h-MoO3),” vol. 50049, p. 50049, 2016.

[131] J. Hamagami, Y. Oh, Y. Watanabe, and M. Takata, “Preparation and characterization of an optically detectable sensor consisting of Pd/MoO, thin films,” vol. 14, pp. 281–283, 1993.